Mass Spectra and Ion Chemistry of Methylphosphine, Dimethylphosphine and Dimethyldeuterophosphine, Investigated by Ion Cyclotron Resonance Spectrometry

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(Z. Naturforsch. **30 a**, 329—339 [1975]; received January 1, 1975)

The mass spectra and the ion molecule reactions of methylphosphine, dimethylphosphine and dimethyldeuterophosphine have been studied by ion cyclotron resonance spectrometry. About 50 ion molecule reaction are observed for each compound. The product ions can be classified as ions with two phosphorus atoms: $P_2R_5^+$, $P_2R_3^+$, $P_2R_2^{\cdot+}$ and P_2R^+ ($R = CH_3$ or H), as phosphonium and phosphinium ions and ions resulting from collision dissociations and charge exchange reactions. Tertiary ions with three phosphorus atoms like $CH_3P_3H_2^+$ (from CH_3PH_2) and $(CH_3)_4P_3H_2$ (from $(CH_3)_2PH$) have also been detected. The mechanisms of the ion molecule reactions, rearrangements, P—H- and C—H-reactivities and product ion structures are discussed, using in the case of dimethylphosphine the results obtained with the deuterated compound. Rate constants of formation of the more abundant product ions from the molecular ion and the $CH_3P^{\cdot+}$ ion, both odd electron particles, have been determined. The reactions with dimethylphosphine have much smaller rate constants than the reactions with methylphosphine.

Introduction

The chemistry of simple organic phosphine derivatives has been established for a long time, a great number of mass spectrometric investigations has been published[1]. However very little is known about the ion chemistry of simple phosphine derivatives. The ion chemistry of phosphine, PH_3, has been studied[2] and recently an investigation of the ion molecule reactions of phosphorus trichloride, phosphoryl chloride and thiophosphorylchloride[3] has been published. In the case of trimethylphosphine the relative proton affinity[4], the basicity[6a] and the ion molecule reactions[5, 6a] have been investigated. The ion chemistry of the two methylfluorophosphines, methyldifluorophosphine and dimethylfluorophosphine has also been studied[6]. Very recently an investigation of the basicity and of some major ion molecule reactions of methylphosphine and dimethylphosphine[6a] has been published. In this work a detailed study of the positive ion chemistry of the two methylphosphines, CH_3PH_2 and $(CH_3)_2PH$, and of the dimethyldeuterophosphine, $(CH_3)_2PD$, which has not been investigated previously, is presented.

Experimental

The experiments have been carried out with the standard ion cyclotron spectrometer Varian V 5900 (Varian Ass. Palo Alto, California), which has been already described in full detail in the literature[7]. Therefore only a brief summary of the experimental details will be given. The spectrometer was equipped with a stainless steel double inlet system and a flat ICR cell measuring $1.25 \times 2.54 \times 16\ \text{cm}^3$, constructed from non-magnetic stainless steel and polyimide rods, allowing a good determination of bimolecular rate constants and single resonance ICR spectra[8]. Recording ICR spectra, electron trap currents were typically in the region of 10^{-7} A, giving total ion currents within the range of 10^{-12} to 10^{-11} A. Therefore disturbance of the ion cyclotron double resonance experiments by space charge and ion trapping are expected to be small[9]. As has been shown recently by Dunbar et al.[10] the changes in ion intensity during double resonance experiments are caused mainly by ion ejection phenomena and/or changes of the rate constants with kinetic energy of the primary ions[7]. Unless otherwise stated, all the spectra were recorded at an electron energy of 30 eV employing an electron energy pulse technique in the mass range $m/e = 2 - 180$. All ions appearing in the single resonance spectra have been subject to double resonance experiments at several sample pressures and irradiating field strengths. Whenever possible the results of the double resonance experiments have been supported by pressure plots.

For a number of ion molecule reactions rate constants have been determined by the method of Goode et al.[11] which has been applied to the measurement of a large number of ion molecule reactions. In this

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approximation the rate constant of formation k_i of i-th secondary ion is given by:

$$k_i = \frac{A_{S,i}\, m_P^2}{m_i^2\,(A_P + m_P^2 \sum\limits_j A_{S,i}/m_j^2)}\; \frac{1}{[M]}\; \frac{1}{t_P' + 2/3\, t_P}$$

where A_P and $A_{S,i}$ and m_P and $m_{S,i}$ are the single resonance intensities and masses of the primary and the i-th secondary ions, M is the number density of the neutral molecules. t_P' and t_P are the times the ions spend in the source and analyzer regions. A plot of

$$A_{S,i}\, m_P^2/m_i^2\,(A_P + m_P^2 \sum_j A_{S,i}/m_j^2)$$

versus pressure gives a straight line with a slope proportional to k_i. The accuracy of the absolute rate constants determined depends on the accuracy of the knowledge of the pressure of the neutral species and the residence times t_P' and t_P of the ions. In this work the pressure has been determined directly from the Vac Ion pump current. The values of t_P' and t_P have been calculated from the known magnetic and electric field strengths. Both procedures yield only approximate values. Therefore the absolute values of the rate constants may be wrong by approximately half their values. However the relative rate constants are much more accurate, we suggest an accuracy of approximately 20%.

Both methylphosphine primary ions yield a great number of product ions. Therefore determination of the rate constants was carried out at several electron energies[12]. At an electron energy of 12 eV (11.5 eV, both values are uncorrected) the only ion to appear is the molecular ion of methylphosphine (dimethylphosphine). In a pressure range from 4×10^{-6} to 2×10^{-5} torr the rate constants of the ion molecule reactions of the molecular ions can now be determined. At a slightly higher electron energy (14.0 eV, uncorrected, in the case of methylphosphine and 13.5 eV, uncorrected, in the case of dimethylphosphine) the $PCH_3^{\cdot +}$ ion, an intense fragment ion, has appeared and its reactions can now be investigated.

In the case of methylphosphine, phosphorus ions resulting from pyrolysis at the hot filament[13, 14] with one, two or four phosphorus atoms show only minor peaks in the spectrum. The ion $m/e = 93$, which is assigned to $P_2(CH_3)_2H^+$, may contain a small fraction of P_3^+ ions, however the relative abundance of this ion does not change if the temperature of the filament is varied, as do the abundances of the ions $m/e = 31$, 62 and 124. The same results are obtained for dimethylphosphine: The ions with $m/e = 31$ and 124 are only minor ions in the spectrum. The molecular ion $m/e = 62$ and the $P_2(CH_3)_2H^+$ ion, $m/e = 93$, may contain a small fraction of $P_2^{\cdot +}$ and P_3^+.

Methylphosphine and dimethylphosphine have been prepared by methods described already in the literature[1] and purified by trap-to-trap condensation in a high vacuum apparatus. The samples did not contain any impurities detectable by the ICR spectrometer. To prevent decomposition the samples have been stored in vacuo at liquid nitrogen temperature.

Results and Discussion

ICR Spectra of Methylphosphine and Dimethylphosphine

Two mass spectrometric investigations of methylphosphine[15, 16] and one of dimethylphosphine[16] are to be found in the literature. They are compared with the ICR spectrometric measurements in Table 1.

Tab. 1. ICR spectra of Methylphosphine and Dimethylphosphine.

		CH_3PH_2 relative abundances		
m/e	ion	ICR spectrum 30 eV	Wada and Kiser[15] 70 eV	Halman[16] 62 eV
15	CH_3^+	20	797	275
29	$C_2H_5^+$	10		359
31	P^+	29		30.2
32	$PH^{\cdot +}$	105		
33	PH_2^+	34		
34	$PH_3^{\cdot +}$	40		
43	CP^+	0	83	13.7
44	$HCP^{\cdot +}$	407	426	6.3
45	H_2CP^+	680	566	1000
46	$H_3CP^{\cdot +}$	1000	1000	484
47	H_3CPH^+	156	158	13.2
48	$H_3CPH_2^{\cdot +}$	806	637	1.0
		$(CH_3)_2PH$		
15	CH_3^+	0		17.6
29	$C_2H_5^+$	0		14.3
31	P^+	0		18.2
32	$PH^{\cdot +}$	0		38.8
33	PH_2^+	0		36.4
34	$PH_3^{\cdot +}$	0		81.3
43	CP^+	0		21.8
44	$HCP^{\cdot +}$	129		140.5
45	H_2CP^+	459		438
46	$H_3CP^{\cdot +}$	1000		1000
47	H_3CPH^+	161		172.5
57	$(CH)_2P^+$	164		146.2
58	$C_2H_3P^{\cdot +}$	57		55
59	$(CH_2)_2P^+$	213		229
61	$(CH_3)_2P^+$	122		140.5
62	$(CH_3)_2PH^{\cdot +}$	596		606

Methylphosphine: Most of the peaks in the ICR spectrum recorded at a pressure of 5×10^{-7} torr and in the mass spectrum reported by Wada and Kiser[15] compare well. The less abundant ions in the mass range $m/e = 31 - 34$ are not given in the cited spectrum, they are however not uncommon. An ion, $m/e = 43$, CP^+, does not appear in the ICR spectrum. The CH_3^+ ion, $m/e = 15$, found as a highly abundant ion in the cited mass spectrum is only a less abundant ion in the ICR spectrum even at 70 eV electron energy. The mass spectrum of Halman[16] does neither agree with our ICR spectrum nor with the mass spectrometric measurements already discussed. Halman found another parent peak, $m/e = 45$ instead of $m/e = 46$. The molecular ion is almost completely missed in his measurements.

Dimethylphosphine: The more abundant ions of our ICR spectrum recorded at a pressure of 5×10^{-7} torr and the mass spectrum of Halman[16] compare well. However the less abundant ions in the mass range $m/e = 15 - 43$ are not detected in the ICR spectrum at low pressures. The parent ion is the $CH_3P^{\cdot +}$ ion, the same ion as in the case of methylphosphine.

By raising the pressure, the ICR spectra of both compounds change, because numerous product ions appear. Figure 1 shows an ICR spectrum of methylphosphine recorded at 5×10^{-6} torr, Fig. 2 shows a spectrum of dimethylphosphine, recorded at 7×10^{-6} torr. Almost all product ions appearing at pressures lower than approximately 3×10^{-5} torr are detected in the mass ranges covered by the figures. At higher pressures new high order product ions begin to appear.

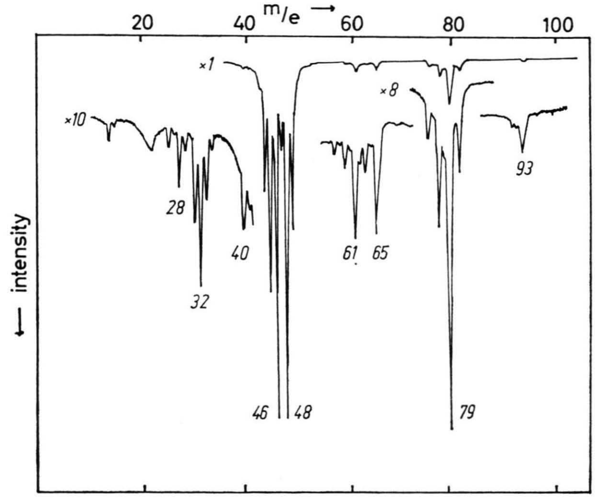


Fig. 1. ICR spectrum of methylphosphine at a pressure of 5×10^{-6} torr and an electron energy of 30 eV.

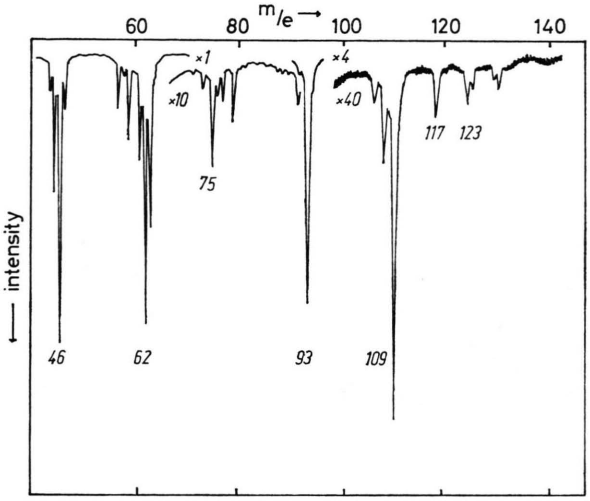


Fig. 2. ICR spectrum of dimethylphosphine at a pressure of 7×10^{-6} torr and an electron energy of 30 eV.

Pressure Dependence of the Relative Intensities

Methylphosphine: The pressure dependences of the mass-corrected relative intensities of all major and minor ions agree well with the results published recently by Staley and Beauchamp[6a] and will therefore not be discussed again. Only two small differences have been observed: The cited authors found the relative intensity of the product ion $m/e = 79$ greater by a factor of approximately two in the whole pressure range covered. The maximum in the intensity-pressure plot detected for the ion $m/e = 47$ by Staley and Beauchamp is not observed in this study.

Dimethylphosphine: The pressure dependences of the mass-corrected relative intensities are shown in Figures 3 and 4. – The good agreement between this work and that of Staley and Beauchamp mentioned above is not observed. Contrary to Staley and Beauchamp the proportion of the protonated molecular ion is found to be much smaller than in the case of methylphosphine. There are also great differences in the intensity-pressure plots of the less abundant product ions. None of the maxima detected by Staley and Beauchamp for the

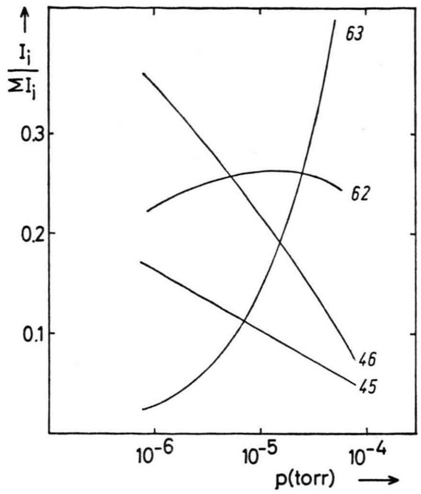


Fig. 3. Mass-corrected relative intensities of the major ions in the ICR spectrum of dimethylphosphine as a function of the total pressure.

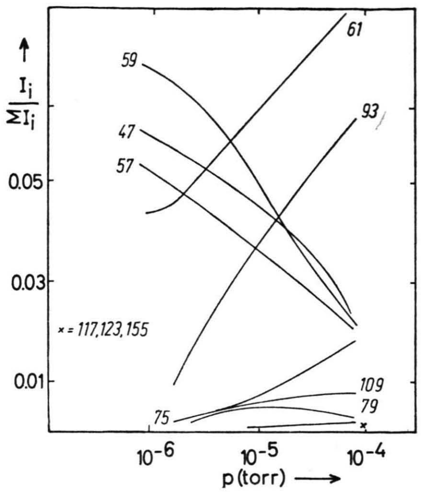


Fig. 4. Mass-corrected relative intensities of the low abundant ions in the ICR spectrum of dimethylphosphine as a function of the total pressure.

ions $m/e=61$, 75 and 93 have been observed. The only ion having a relative intensity passing through a maximum if the pressure is raised is the minor ion $m/e=79$, not shown in the cited plot. Besides the protonated molecule in this study only three product ions are observed to have relative abundances greater than 1%: the dimethylphosphonium ion, $m/e=61$, also appearing as a less abundant primary ion, the $P_2(CH_3)_2H^+$ ion, $m/e=93$ and the $(CH_3)_2PCH_2{}^+$ ion, $m/e=75$.

Ion Molecule Reactions

The ion molecule reactions of the methylphosphines can be devided into four reaction types already known from chemistry, as it has been possible in the case of trimethylphosphine [5] and methyldifluorophosphine and dimethylfluorophosphine [6]:

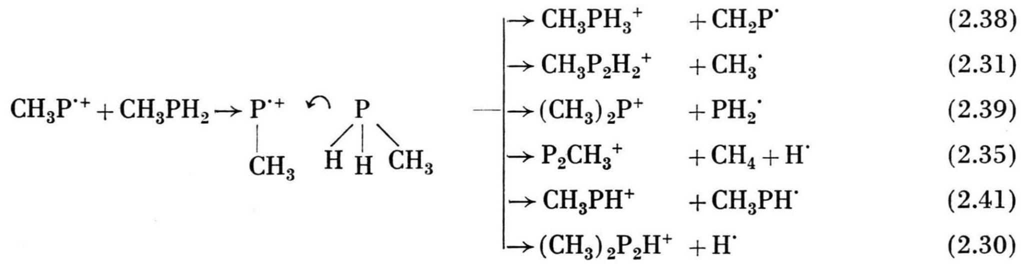
1. reactions yielding phosphonium ions with two or three phosphorus atoms,
2. reactions yielding quasi phosphonium and phosphonium ions with one phosphorus atom,
3. collision-induced dissociations,
4. charge exchange reactions.

According to this scheme the ion molecule reactions of methylphosphine will be discussed first, followed by a discussion of the ion molecule reactions of dimethylphosphine. A third part is dedicated to the discussion of reaction mechanisms and product ion structures while in a fourth part some quantitative results will be presented.

Methylphosphine: All the ion molecule reactions of the primary ion detected in the pressure range from 10^{-7} to 10^{-4} torr are listed in Table 2. The formation reactions of the more abundant ions are found to be in good agreement with those published recently by Staley and Beauchamp. Therefore they will only be discussed briefly (Reactions 2.10, 2.18, 2.31, 2.38, 2.39, 2.46, 2.48, 2.51).

The methylphosphonium ion which is the most abundant product ion is formed exclusively by reactions of the molecular ion (2.18), the $CH_3P^{\cdot +}$ ion (2.38) and the CH_2P^+ ion (2.51). Reactions (2.38) and (2.51) are proton transfer reactions. The formation reaction of the protonated molecule from the molecular ion is also believed to be a proton transfer, because this reaction is analogous to the reactions of the fragment ions.

The three primary ions yielding the protonated molecule have however a lot of further reaction pathways. The primary step in all these reactions is thought to be a nucleophilic attack by the phosphorus atom of the neutral molecule at the phosphorus atom of the ion, resulting in an intermediate which has several further reaction pathways. This is illustrated by the reactions of the $CH_3P^{\cdot +}$ ion:



$$CH_3P^{\cdot+} + CH_3PH_2 \rightarrow \underset{CH_3}{P^{\cdot+}} \curvearrowleft \underset{H\ H\ CH_3}{P} \left\{ \begin{array}{lll} \rightarrow CH_3PH_3^+ & + CH_2P^{\cdot} & (2.38) \\ \rightarrow CH_3P_2H_2^+ & + CH_3^{\cdot} & (2.31) \\ \rightarrow (CH_3)_2P^+ & + PH_2^{\cdot} & (2.39) \\ \rightarrow P_2CH_3^+ & + CH_4 + H^{\cdot} & (2.35) \\ \rightarrow CH_3PH^+ & + CH_3PH^{\cdot} & (2.41) \\ \rightarrow (CH_3)_2P_2H^+ & + H^{\cdot} & (2.30) \end{array} \right.$$

The $CH_3P^{\cdot+}$ ion reacts mainly as a proton transfer (2.38) or a phosphorus cation transfer reagent (2.31) or as an acceptor of a methyl group (2.39). Minor reactions are the acceptance of phosphorus (2.35) or a hydrogen atom (2.41) from the neutral molecule. A further possible reaction pathway is the stabilization of the intermediate by dissociation of an H-atom (2.30). In most of these reactions only $P-H$- and $P-C$-bonds are believed to dissociate. The abundance of product ions formed by reactions which can be regarded as simple transfer reactions of an ion or an atom including dissociation of only one chemical bond is in most cases greater than the abundance of product ions formed by reactions including dissociation of several chemical bonds. Ion transfer is normally more probable than atom transfer. The other reactions of the $CH_3P^{\cdot+}$ ion listed in Table 2 can only be interpreted assuming dissociation of at least one $C-H$-bond in the reaction intermediate.

Two further formation reactions of the dimethylphosphinium ion have been detected:

$$CH_3PH_2^{\cdot+} + CH_3PH_2 \rightarrow (CH_3)_2P^+ + (PH_3 + H^{\cdot}), \qquad (2.19)$$

$$CH_3PH^+ + CH_3PH_2 \rightarrow (CH_3)_2P^+ + PH_3\,. \qquad (2.27)$$

The main formation reaction of the secondary ion $(CH_2)_2P^+$, $m/e = 59$, is the reaction of the CH_2P^+ ion with the neutral molecule:

$$CH_2P^+ + CH_3PH_2 \rightarrow (CH_2)_2P^+ + PH_3\,. \qquad (2.52)$$

Moreover the $(CH_2)_2P^+$ ion is formed by all primary ions having at least two $C-H$-bonds. Also the secondary ion $C_2H_2P^+$ is observed.

In the case of methylphosphine the product ions with two phosphorus atoms can be devided into two groups: the low abundant ions $m/e = 63$, 64, and 65, $P_2H_x^+$ $(x = 1, 2, 3)$ containing only hydrogen-phosphorus-bonds and ions containing at least one carbon atom bonded to phosphorus. The two more abundant diphosphine ions P_2H^+ and $P_2H_3^+$ are formed by ion molecule reactions of the CH_2P^+ ion with the neutral methylphosphine:

$$CH_2P^+ + CH_3PH_2 \rightarrow P_2H_3^+ + C_2H_4\,, \qquad (2.46)$$

$$CH_2P^+ + CH_3PH_2 \rightarrow P_2H^+ + C_2H_6\,. \qquad (2.49)$$

The neutral particles formed are ethene and ethane respectively. As can be expected, the $P_2H_2^{\cdot+}$ ion is not formed from CH_2P^+ but from $CH_3P^{\cdot+}$:

$$CH_3P^{\cdot+} + CH_3PH_2 \rightarrow P_2H_2^{\cdot+} + C_2H_6\,. \qquad (2.34)$$

The CH_2P^+ ion plays also an important role in the formation reactions of diphosphine ions with at least one carbon atom bonded to phosphorus. The two secondary ions P_2CH^+, $m/e = 75$ and $P_2CH_3^+$, $m/e = 77$, are mainly formed by ion molecule reactions of the CH_2P^+ ion:

$$PCH_2^+ + CH_3PH_2 \rightarrow P_2CH^+ + CH_4 + H_2\,, \qquad (2.50)$$

$$PCH_2^+ + CH_3PH_2 \rightarrow P_2CH_3^+ + CH_4\,. \qquad (2.48)$$

Again, very stable neutral particles, methane or hydrogen, are formed. As can be expected, the $P_2CH_3H^{\cdot+}$ ion is formed by an ion molecule reaction of the $PCH_3^{\cdot+}$ ion:

$$PCH_3^{\cdot+} + CH_3PH_2 \rightarrow P_2CH_3H^{\cdot+} + CH_4\,. \qquad (2.47)$$

As has been shown above, the $CH_3P^{\cdot+}$ ion is a powerful phosphorus cation transfer reagent. The CH_2P^+ ion also transfers phosphorus, however complicated rearrangements are taking place in the course of its reactions. At pressures higher than 1.5×10^{-5} torr, the molecular ion becomes also a phosphorus transfer reagent:

$$CH_3PH_2^{\cdot+} + CH_3PH_2 \rightarrow P_2CH_3H_2^+ + CH_4 + H^{\cdot}\,. \qquad (2.11)$$

Table 2. Product ions of the ion molecule reactions of the ions of methylphosphine.

Reacting ions Product ions	$PCH_3H_3^+$	Nr.	$PCH_3H_2^{\cdot+}$	Nr.	PCH_3H^+	Nr.	$PCH_3^{\cdot+}$	Nr.	PCH_2^+	Nr.	$PCH^{\cdot+}$	Nr.	$PH^{\cdot+}$	Nr.	P^+	Nr.
1. diphosphine ions																
$P_2R_5^+$	$P_2CH_3H_4^+$	1	$P_2CH_3H_4^+$	10												
$P_2R_3^+$					$P_2(CH_3)_2H^+$	25	$P_2(CH_3)_2H^+$	30								
	$P_2CH_3H_2^+$	2	$P_2CH_3H_2^+$	11			$P_2CH_3H_2^+$	31	$P_2CH_3H_2^+$	45	$P_2CH_3H_2^+$	57				
	$P_2H_3^+$	3	$P_2H_3^+$	12			$P_2H_3^+$	32	$P_2H_3^+$	46	$P_2H_3^+$	58	$P_2H_3^+$	63		
$P_2R_2^{\cdot+}$	$P_2CH_3H^{\cdot+}$	4	$P_2CH_3H^{\cdot+}$	13			$P_2CH_3H^{\cdot+}$	33	$P_2CH_3H^{\cdot+}$	47	$P_2CH_3H^{\cdot+}$	59				
			$P_2H_2^{\cdot+}$	14			$P_2H_2^{\cdot+}$	34							$P_2H_2^{\cdot+}$	64
P_2R^+	$P_2CH_3^+$	5	$P_2CH_3^+$	15			$P_2CH_3^+$	35	$P_2CH_3^+$	48						
			P_2H^+	16			P_2H^+	36	P_2H^+	49						
	P_2CH^+	6	P_2CH^+	17	P_2CH^+	26	P_2CH^+	37	P_2CH^+	50						
2. phosphine ions																
PR_4^+			$PCH_3H_3^+$	18			$PCH_3H_3^+$	38	$PCH_3H_3^+$	51						
PR_2^+	$P(CH_3)_2^+$	7	$P(CH_3)_2^+$	19	$P(CH_3)_2^+$	27	$P(CH_3)_2^+$	39								
	$P(CH_2)_2^+$	8	$P(CH_2)_2^+$	20	$P(CH_2)_2^+$	28	$P(CH_2)_2^+$	40	$P(CH_2)_2^+$	52						
	$P(CH)_2^+$	9	$P(CH)_2^+$	21					$P(CH)_2^+$	53	$P(CH)_2^+$	60				
							PCH_3H^+	41								
$PR^{\cdot+}$									$PCH_3^{\cdot+}$	54	$PCH_3^{\cdot+}$	61				
3. Collision			PCH_3H^+	22												
dissociation			$PCH_3^{\cdot+}$	23	$PCH_3^{\cdot+}$	29										
			PCH_2^+	24			PCH_2^+	42	$PCH^{\cdot+}$	55						
4. Charge							$PCH^{\cdot+}$	43	$PCH_3H_2^{\cdot+}$	56						
exchange							$PCH_3H_2^{\cdot+}$	44			$PCH_3H_2^{\cdot+}$	62				

Only one secondary ion with the general formula $P_2R_5^+$ has been observed, the $P_2CH_3H_4^+$ ion, formed in the reaction (2.10) by the molecular ion. This ion is also formed as a tertiary ion by a reaction of the protonated molecule:

$$CH_3PH_3^+ + CH_3PH_2 \rightarrow CH_3P_2H_4^+ + CH_4 \,. \qquad (2.1)$$

This reaction may be regarded as an analogue to the clustering reactions found by Long and Franklin[17] in the case of posphine by high pressure mass spectrometry:

$$PH_4^+ + PH_3 \rightarrow PH_4^+ \cdot PH_3 \rightarrow P_2H_5^+ + H_2 \,.$$

The intermediate $P_2H_7^+$ ion dissociates at room temperature into the $P_2H_5^+$ ion and a hydrogen molecule but is stable below room temperature.

Several further tertiary ions are formed with low abundance in the course of ion molecule reactions of the protonated molecule. They are listed in Table 2. Only one tertiary ion with three phosphorus atoms has been observed at pressures below 10^{-4} torr:

$$CH_3P_2H_2^+ + CH_3PH_2 \rightarrow CH_3P_3H_2^{\cdot+} + (CH_4 + H^{\cdot}) \,. \qquad (1)$$

At pressures above 10^{-4} torr two further product ions become detectable in the mass range covered, the ions with $m/e = 127$ and 142, tentatively assigned to the structures $(CH_3)_2P_3H_4^+$ and $(CH_3)_3P_3H_4^+$.

Su and Kevan[18] have shown the presence of internally excited ions by an investigation of the line shapes and pressure dependences of double resonance signals. The same effects have been observed for the formation reactions of several product ions of methylphosphine, especially in the case of the formation of the $CH_3P_2H_2^+$ ion, suggesting that at least some of the ions CH_3PH_3, $CH_3PH_2^{\cdot+}$, $CH_3P^{\cdot+}$, CH_2P^+ and $CHP^{\cdot+}$ may exist in excited states at low pressures. Further studies concerning this problem are in progress[19].

Dimethylphosphine and dimethyldeuterophosphine: The ion molecule reactions detected in the pressure range from 10^{-7} to 10^{-4} torr are listed in Table 3. The formation reactions of some more abundant ions have already been investigated by Staley and Beauchamp[6a] (reactions 3.2, 3.9, 3.17, 3.20, 3.30, 3.32, 3.35, 3.36, 3.44). They are found to be in good qualitative agreement with this study. Therefore the ion chemistry of dimethylphosphine will be discussed in the light of the results obtained with the deuterated analogue.

The protonated molecule is formed by five ion molecule reactions (3.9), (3.16), (3.29), (3.35) and (3.43). The last four reactions are evidently proton transfer reactions. Therefore also the reaction occurring in a mixture of dimethylphosphine and dimethyldeuterophosphine

$$(CH_3)_2PH^{\cdot+} + (CH_3)_2PD \rightarrow (CH_3)_2PDH^+ + (CH_3)_2P^{\cdot} \quad (3.9\,a)$$

is believed to be a proton transfer and not a deuterium atom transfer.

The secondary ion with $m/e = 75$ has the composition $(CH_3)_2PCH_2^+$. It is formed by several ion molecule reactions:

$$HPCH_3^+ + (CH_3)_2PD \rightarrow (CH_3)_2PCH_2^+ + PH_2D\,, \quad (3.30\,a)$$

$$DPCH_3^+ + (CH_3)_2PD \rightarrow (CH_3)_2PCH_2^+ + PHD_2\,, \quad (3.30\,b)$$

$$CH_3P^{\cdot+} + (CH_3)_2PD \rightarrow (CH_3)_2PCH_2^+ + PDH^{\cdot}\,. \quad (3.36\,a)$$

Supposing that the ion $m/e = 76$ consists at least in part of $PC_3H_7D^+$, its formation reaction is:

$$DPCH_3^+ + (CH_3)_2PD \rightarrow PC_3H_7D^+ + PH_2D \quad (3.30\,c)$$

and not

$$HPCH_3^+ + (CH_3)_2PD \not\rightarrow PC_3H_7D^+ + PH_3\,.$$

All reactions show a complicated mechanism with P – H- (P – D-) and C – H-bond dissociation.

All three possible compositions of $P_2R_3^+$ ions ($R = CH_3$ or H) have been formed by ion molecule reactions without C – H-bond dissociation. The abundances of the product ions decreases strongly in the order:

$$(CH_3)_2P_2H^+ > CH_3P_2H_2^+ > (CH_3)_3P_2^+\,.$$

As can be expected these ions are formed by the already discussed phosphorus transfer reagents $PCH_3^{\cdot+}$ and PCH_2^+:

$$CH_3P^{\cdot+} + (CH_3)_2PH \rightarrow (CH_3)_2P_2H^+ + CH_3^{\cdot}\,, \quad (3.32)$$

$$CH_2P^+ + (CH_3)_2PH \rightarrow CH_3P_2H_2^+ + C_2H_4\,. \quad (3.40)$$

However a third phosphorus transfer reagent already known from the ion chemistry of trimethylphosphine [5] has been observed, the $P(CH_2)_2^+$ ion:

$$(CH_2)_2P^+ + (CH_3)_2PH \rightarrow (CH_3)_2P_2H^+ + C_2H_4\,. \quad (3.20)$$

The $(CH_3)_3P_2^+$ ion is a tertiary and not a secondary ion:

$$(CH_3)_2P_2H^+ + (CH_3)_2PH \rightarrow (CH_3)_3P_2^+ + CH_3PH_2\,. \quad (2)$$

The corresponding reaction of the deuterated analogue is:

$$(CH_3)_2P_2D^+ + (CH_3)_2PD \rightarrow (CH_3)_3P_2^+ + CH_3PD_2\,. \quad (2\,a)$$

Only two different ions with the general formula $P_2R_5^+$ have been detected in the spectrum. The more abundant one, the $(CH_3)_3P_2H_2^+$ ion, $m/e = 109$, is formed by a displacement reaction:

$$(CH_3)_2PH^{\cdot+} + (CH_3)_2PH \rightarrow (CH_3)_3P_2H_2^+ + CH_3^{\cdot}\,. \quad (3.2)$$

Much less abundant is the ion with $m/e = 123$, formed by a condensation reaction of the molecular ion (3.1) and an addition reaction of the dimethylphosphinium ion (3.15):

$$(CH_3)_2PH^{\cdot+} + (CH_3)_2PH \rightarrow (CH_3)_4P_2H^+ + H^{\cdot}\,, \quad (3.1)$$

$$(CH_3)_2P^+ + (CH_3)_2PH \rightarrow (CH_3)_4P_2H^+\,. \quad (3.15)$$

In the case of the deuterated compound the corresponding reactions are observed. The ion $m/e = 123$ is therefore believed to have the composition $(CH_3)_4P_2H^+$ and not $(CH_3)_2P_3^+$ as has been proposed by Staley and Beauchamp, who have detected a formation reaction from the secondary ion $(CH_3)_2P_2H^+$, having not been observed in the present study.

The ion with $m/e = 117$ is formed by reactions of the $(CH)_2P^+$ ion exclusively:

$$(CH)_2P^+ + (CH_3)_2PH \rightarrow P_2C_4H_7^+ + H_2\,, \quad (3.26)$$

$$(CH)_2P^+ + (CH_3)_2PD \rightarrow P_2C_4H_7^+ + HD\,. \quad (3.26\,a)$$

Again the P – D-bond is dissociated.

The $(CH_3)_2P_2H^+$ ion forms two tertiary ions with three phosphorus atoms, a minor ion, $m/e = 139$, $P_3C_3H_{10}^+$, already detected by Staley and Beauchamp, and a major ion, $m/e = 155$, by an addition reaction:

$$(CH_3)_2P_2H^+ + (CH_3)_2PH \rightarrow (CH_3)_4P_3H_2^+ \quad (3)$$

which can be written as $P[(CH_3)_2PH]_2^+$.

Table 3. Product ions of the ion molecule reactions of the

Primary ions Product ions	$P(CH_3)_2H^{\cdot+}$	Nr.	$P(CH_3)_2^+$	Nr.	$P(CH_2)_2^+$	Nr.	$C_2H_3P^{\cdot+}$	Nr.
1. diphosphine ions								
$P_2R_5^+$	$P_2(CH_3)_4H^+$	1	$P_2(CH_3)_4H^+$	15				
	$P_2(CH_3)_3H_2^+$	2						
$P_2R_3^+$							$P_2(CH_3)C_2H_3H^+$	24
	$P_2(CH_3)_2H^+$	3			$P_2(CH_3)_2H^+$	20		
	$P_2C_3H_4^+$	4						
	$P_2CH_3H_2^+$	5			$P_2CH_3H_2^+$	21		
	$P_2H_3^{\cdot+}$	6						
$P_2R_2^{\cdot+}$	$P_2H_2^{\cdot+}$	7						
P_2R^+	$P_2CH_3^+$	8						
2. phosphine ions								
PR_4^+	$P(CH_3)_2H_2^+$	9	$P(CH_3)_2H_2^+$	16				
$PR_3^{\cdot+}$							$P(CH_3)_3^{\cdot+}$	25
	$P(CH_3)_2CH_2^+$	10	$P(CH_3)_2CH_2^+$	17				
PR_2^+								
3. collision dissociation	$P(CH_3)_2^+$	11						
	$P(CH_2)_2^+$	12	$P(CH_2)_2^+$	18				
	$P(CH)_2^+$	13			$P(CH)_2^+$	22		
	$PCH_3^{\cdot+}$	14	$PCH_3^{\cdot+}$	19				
4. charge exchange					$P(CH_3)_2H^{\cdot+}$	23		

Reaction Mechanisms and Structures of Product Ions

The ion molecule reactions of the two methylphosphines studied are thought to proceed via the same mechanism, already discussed in the case of the reactions of the $CH_3P^{\cdot+}$ ion with methylphosphine, a nucleophilic attack by the phosphorus of the neutral molecule at the phosphorus atom of the ion:

$$R_nP^+ + PR_3 \rightarrow R_nP^{+\curvearrowleft}PR_3 \rightarrow \text{products}\,. \qquad (4)$$

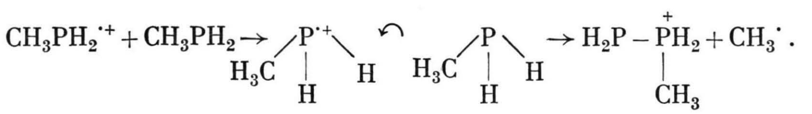
The lifetime of this intermediate must be short compared with the time necessary to detect the ions in the ICR cell, because the intermediate has never been observed by double resonance experiments. Addition products are in general unstable in the case of methylphosphine and dimethylphosphine.

Contrary to trimethylphosphine[5] no dimeric molecular ions have been found in the pressure range studied and no secondary ions formed by addition reactions have been observed. The unstable intermediate dissociates into the final product ion and one or two small neutral particles.

The simple alkylphosphines are known from organic phosphorus chemistry to react as strong nucleophiles[20, 21]. Tetramethyldiphosphine is readily formed by a reaction of dimethylphosphine and dimethylchlorophosphine[22]. A synthesis of methyldiphosphine and of 1.2-dimethyldiphosphine from methylphosphine using an electric discharge method has been recently described[23]. The tetramethydiphosphine can be quarternized by methyliodide[24, 25], pentamethyldiphosphonium(+1)-ions are formed. Therefore the product ions with two phosphorus atoms are thought to have diphosphonium ion structures with a phosphorus-phosphorus-bond.

Three of the five possible $P_2R_5^+$ ions ($R = CH_3$ or H) have been detected. $CH_3P_2H_4^+$ and $(CH_3)_3P_2H_2^+$ ions are formed by the displacement reactions (2.10) and (3.2).

If no rearrangement takes place, the most probable structure of the $CH_3P_2H_4^+$ ions is $H_2PPH_2CH_3^+$:

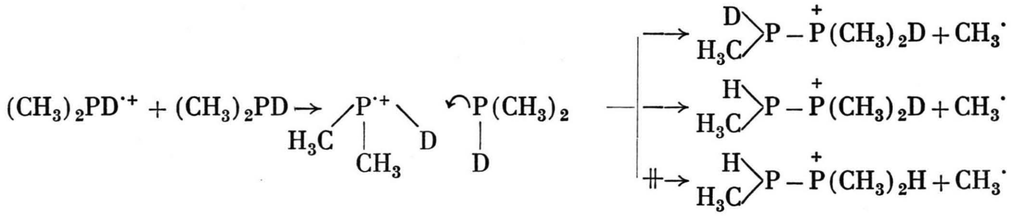


$$CH_3PH_2^{\cdot+} + CH_3PH_2 \rightarrow \underset{H_3C\;\;\;\;H\;\;\;\;H}{P^{\cdot+}} \curvearrowleft \underset{H_3C\;\;\;\;H\;\;\;\;H}{P} \rightarrow H_2P-\overset{+}{P}H_2(CH_3) + CH_3^{\cdot}\,. \qquad (2.10)$$

primary ions of dimethylphosphine.

$(CH)_2P^+$	Nr.	$CH_3PH^{\cdot +}$	Nr.	$CH_3P^{\cdot +}$	Nr.	CH_2P^+	Nr.
$P_2C_4H_7^+$	26						
				$P_2(CH_3)_2H^+$	32	$P_2(CH_3)_2H^+$	40
$P_2C_3H_4^+$	27						
						$P_2CH_3H_2^+$	41
				$P_2H_3^+$	33		
$P_2CH_3^+$	28			$P_2CH_3^+$	34	$P_2CH_3^+$	42
		$P(CH_3)_2H_2^+$	29	$P(CH_3)_2H_2^+$	35	$P(CH_3)_2H_2^+$	43
		$P(CH_3)_2CH_2^+$	30	$P(CH_3)_2CH_2^+$	36		
				$P(CH_3)_2^+$	37	$P(CH_3)_2^+$	44
				$P(CH_2)_2^+$	38		
		$PCH_3^{\cdot +}$	31				
				$P(CH_3)_2H^{\cdot +}$	39	$P(CH_3)_2H^{\cdot +}$	45

There are several structures possible for the $(CH_3)_3P_2H_2^+$ ion. Experiments with the deuterated dimethylphosphine strongly indicate a reaction without rearrangement in the neutral molecule:



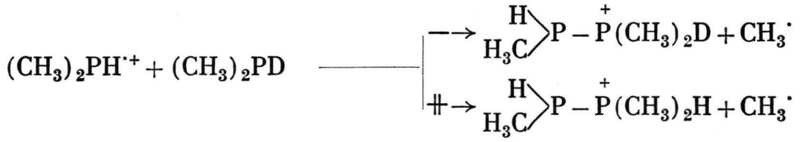
(3.2 a)

(3.2 b)

The sum of the rate constants of reactions (3.2 a) and (3.2 b) has been measured:

$$k_{3.2a} + k_{3.2b} = 0.07 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ sec^{-1}}.$$

The corresponding reaction of a mixture of $(CH_3)_2PH$ and $(CH_3)_2PD$ supports this result:

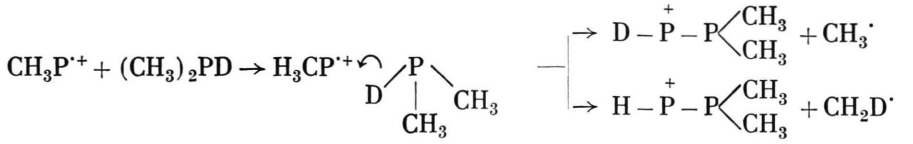


(3.2 c)

(3.2 d)

Therefore the structure of the trimethyldiphosphonium ion will be: $CH_3(H)PPH(CH_3)_2^+$. Reactions (3.2a) and (3.2 b) indicate scrambling of the hydrogen atoms in the primary ion. The course of the ion molecule reactions discussed indicates scrambling during primary ion formation and not during the ion molecule reaction. The ratio of the product ions $(CH_3)_3P_2D_2^+$ and $(CH_3)_3P_2HD^+$ is approximately 2 : 1, indicating an incomplete scrambling. However this question needs further investigation.

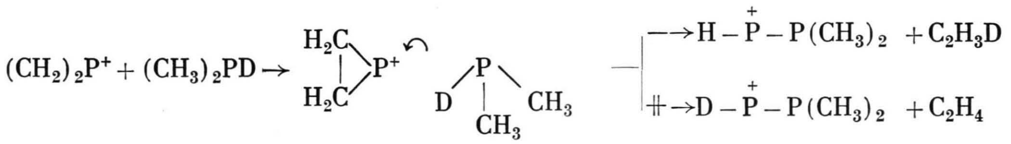
Three of the four possible ions with the general formula $P_2R_3^+$, $P_2H_3^+$, $CH_3P_2H_2^+$ and $(CH_3)_2P_2H^+$ are formed as secondary ions. There are two possible structures with a phosphorus-phosphorus-bond: The PPR_3^+ ions can be formed without rearrangement, $RPPR_2^+$ ions can only be formed after rearrangement has taken place in the reaction complex. Reaction of the $CH_3P^{\cdot +}$ ion with the deuterated dimethylphosphine strongly indicates rearrangement, including C – H-bond dissociation:



(3.32 a)

(3.32 b)

The positions of the H-atom and the methyl groups are not proved. The reaction of the $(CH_2)_2P^+$ ion indicates also a complicated mechanism:



(3.20 a)

Evidently the phosphorus cation transfer reagents $CH_3P^{\cdot +}$ and $(CH_2)_2P^+$ have different reaction mechanisms. The difference can be rationalized with the different structures of the $CH_3P^{\cdot +}$ and $(CH_2)_2P^+$ ions: The last-named is assumed to have a cyclic structure [5]. The molecular ion which shows also a minor phosphorus transfer reaction reacts like the $CH_3P^{\cdot +}$ ion. Both ions are odd electron ions.

In general the most intense product ions result, if a methylgroup is formed as the neutral particle during the course of the formation reactions of ions with the general formulas $P_2R_3^+$ and $P_2R_5^+$.

Quantitative Results

Formation of the Protonated Molecular Ions

The main formation reactions are the proton transfer reactions by the molecular ion and the $CH_3P^{\cdot +}$ ion:

$$CH_3PH_2^{\cdot +} + CH_3PH_2 \xrightarrow{k_{2.18}=8.2} CH_3PH_3^+ + CH_3PH^{\cdot}, \qquad (2.18)$$

$$CH_3P^{\cdot +} + CH_3PH_2 \xrightarrow{k_{2.38}=3.7} CH_3PH_3^+ + CH_2P^{\cdot}, \qquad (2.38)$$

$$(CH_3)_2PH^{\cdot +} + (CH_3)_2PH \xrightarrow{k_{3.9}=1.4} (CH_3)_2PH_2^+ + C_2H_6P^{\cdot}, \qquad (3.9)$$

$$CH_3P^{\cdot +} + (CH_3)_2PH \xrightarrow{k_{3.35}=0.1} (CH_3)_2PH_2^+ + CH_2P^{\cdot}. \qquad (3.35)$$

The rate constants are given in units of 10^{-10} cm^3 $molecule^{-1}$ sec^{-1}. The rate constants of formation of the phosphonium ions increase with an increasing number of P – H-bonds in the neutral phosphine. Beauchamp and coworkers [2] have determined the rate constant of the corresponding reaction of phosphine:

$$PH_3^{\cdot +} + PH_3 \xrightarrow{k_5=10.5} PH_4^+ + PH_2^{\cdot} \qquad (5)$$

which fits well in this order. Also the rate constant of reaction (2.18) agrees well with the value of 8.8×10^{-10} cm $molecule^{-1}$ sec^{-1} determined by Staley and Beauchamp [6a]. However there exists a severe difference for the rate constant of reaction (3.9), which is given as 6.0×10^{-10} cm^3 $molecule^{-1}$ sec^{-1} in the cited publication. This difference is much greater than uncertainties caused by the pressure measurement and cannot be rationalized. There should be a strong decrease in the rate constants of formation of the protonated molecular ions from the molecular ions with an increasing number of methylgroups [5]. Therefore the rate constant of reaction (3.9) should be smaller than 6.0 cm^3 $molecule^{-1}$ sec^{-1}.

The ratio of the rate constants of formation of $(CH_3)_2PD_2^+$ and $(CH_3)_2PHD^+$ by ion molecule reactions of dimethyldeuterophosphine, corresponding to reaction (3.9)

$$(CH_3)_2PD^{\cdot +} + (CH_3)_2PD \begin{cases} \xrightarrow{k_{3.9a}} (CH_3)_2PD_2^{+} + (CH_3)_2P^{\cdot} & (3.9\,a) \\ \xrightarrow{k_{3.9b}} (CH_3)_2PDH^{+} + C_2H_5DP^{\cdot} & (3.9\,b) \end{cases}$$

has been determined:

$$k_{3.9\,a}/k_{3.9\,b} = 2.3$$

showing that the P – D-bond reacts 2.3 times faster a C – H-bond. The P – H-bonds however influence the reaction rate constants of C – H-bonds: The rate constant of reaction (3.35) is smaller than the rate constant, which may be roughly estimated from the given ratio $k_{3.9a}/k_{3.9b}$, neglecting isotope effects.

Formation of Diphosphonium Ions

The rate constants of the major reactions leading to diphosphonium ions have been determined. The reaction of methylphosphine yielding methyldiphosphonium(+1) ions

$$CH_3PH_2^{\cdot +} + CH_3PH_2 \xrightarrow{k_{2.1}=0.39} CH_3P_2H_4^{+} + CH_3^{\cdot} \quad (2.10)$$

has a greater rate constant than the corresponding reaction of the dimethylphosphine:

$$(CH_3)_2PH^{\cdot +} + (CH_3)_2PH \xrightarrow{k_{3.2}=0.07} (CH_3)_3P_2H_2^{+} + CH_3^{\cdot}\,. \quad (3.2)$$

As in the case of the formation of the protonated molecules the rate constant of reaction (2.10) agrees better with the value of 0.7×10 cm^3 molecule^{-1} sec^{-1} given by Staley and Beauchamp [6a] than those of reaction (3.2) given as 0.3 cm^3 molecule^{-1} sec^{-1} in the cited literature. The fact that the ion molecule reactions of methylphosphine have greater rate constants than those of dimethylphosphine has already been observed in the case of the protonation reactions discussed above. The same is true for the formation reactions of the ions $P_2R_3^{+}$ by the phosphorus cation transfer reagent $CH_3P^{\cdot +}$:

$$CH_3P^{\cdot +} + CH_3PH_2 \xrightarrow{k_{2.31}=2.3} CH_3P_2H_2^{+} + CH_3^{\cdot}\,, \quad (2.31)$$

$$CH_3P^{\cdot +} + (CH_3)_2PH \xrightarrow{k_{3.32}=0.13} (CH_3)_2P_2H^{+} + CH_3^{\cdot}\,. \quad (3.32)$$

Acknowledgements

The author thanks Professor H. Hartmann for his encouraging support and the permission to use the research facilities which have been made available to Prof. Hartmann by the Deutsche Forschungsgemeinschaft.

The author expresses his appreciation to Dr. G.-V. Röschenthaler and Dipl.-Chem. E. Unger, Lehrstuhl B für Anorganische Chemie der Technischen Universität Braunschweig for samples of the compounds studied in this work.

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